

HIGH-PERFORMANCE PLATINIZED CARBON ELECTRODES FOR OXYGEN REDUCTION IN POWER SOURCES WITH ALKALINE ELECTROLYTES

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Summary

A high-performance, oxygen-reducing electrode, made from physically and chemically tailored coconut-shell charcoal substrate catalyzed with 7 wt.% platinum, is reported. The electrode can be loaded with current densities of 2000 - 5200 A/m², with negligible deterioration, for periods of up to 1200 h. Extensive electron spectroscopic studies have been conducted to characterise the electroactive species present on the surface of the electrodes during service.

Introduction

The development of fuel-cell electrodes has been the focus of intensive efforts for the past two decades. Starting from the pure platinum-black structure of the 1960s and the mixed precious metal catalysts of the early 1970s, present day endeavours are to develop carbon- or graphite-supported catalytic electrodes in order to achieve high power yields per unit weight of catalyst.

In an earlier communication [1], we reported that coconut-shell charcoal is an excellent, low-cost substrate for fabricating carbon-based air electrodes for use in alkaline fuel/air fuel cells and metal/air batteries. It was shown that such electrodes could be loaded with practically acceptable current densities of 500 - 2000 A/m² without deterioration for periods of up to 200 h. It was also noted that, at an appreciably high load current density of 5200 A/m², these electrodes deteriorate slowly after a service of 2 h. The performance of these electrodes is competitive with other carbon-based air electrodes reported in the literature. However, it is imperative to deposit surface catalysts onto these electrodes in order to enhance their electrochemical characteristics. For this purpose, various chemical methods have been employed to obtain fine dispersions of platinum metal

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catalyst on different types of carbon, and metal areas as high as 150 m^2 per gram of the metal have been achieved as against the area of about 30 m^2 per gram of the metal alone [2].

In this communication, we discuss the performance of coconut-shell-charcoal-based-air electrodes catalyzed with 7 wt.% of platinum. The effect of heat-treatment (under vacuum) of the platinum-catalyzed charcoal support on the electrochemical activity of the electrodes is also reported. These catalytic electrodes exhibited a marked enhancement in their electrochemical activity towards oxygen reduction in alkaline media. Unlike the case of bare (*i.e.*, no catalyst) carbon electrodes which were seen to deteriorate after a period of 2 h at load current densities of 5200 A/m^2 [1], negligible deterioration of the platinized carbon electrodes has been observed for the duration ($\sim 1200 \text{ h}$) of the load tests ($2000 - 5200 \text{ A/m}^2$). Indeed, these electrodes could be loaded for short durations at current densities as high as $22\,000 \text{ A/m}^2$ at a potential of $-0.37 \text{ V vs. Hg/HgO, OH}^-$ in 6M KOH electrolyte. This performance is superior to those reported for other platinized-carbon-air electrodes.

Several spectroscopic techniques have been employed [1, 3 - 8] to characterize the electroactive species present on the surface of electrodes. We have carried out a detailed X-ray photoelectron spectroscopic (XPS) study to determine the surface active species responsible for enhancing the electrochemical performance of the platinized-carbon-air electrodes reported here.

Experimental

(i) Deposition of platinum catalyst

Details pertaining to the preparation of active carbon from coconut-shell charcoal by gas activation and its characterization have been described previously [1]. The procedure used for depositing platinum catalyst on this carbon support is as follows. A chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$) solution containing the required amount (in wt.%) of platinum is taken from a 1% stock solution. An amount of isopropanol equal to nearly half the volume of chloroplatinic acid is then added. To this mixture, the appropriate quantity of treated carbon (with 66 wt.% loss on gas activation, preferably first with CO_2 and later with NH_3 at $\sim 900^\circ \text{C}$) is added and mixed thoroughly. The resulting mixture is dried in an air-oven and later heated at about 150°C in air to effect the partial decomposition of chloroplatinic acid to platinum. This is followed by chemical treatment with an appropriate quantity of 1% NaBH_4 solution to ensure complete reduction of chloroplatinic acid to platinum. This process is similar to that described by Scarr and Kordesch [9] for the preparation of platinized-carbon paper electrodes. The resulting mass is filtered, washed repeatedly, and finally dried in the air-oven. The optimum amount of platinum to be deposited on the carbon substrate has been determined by conducting electroactivity tests on electrodes containing

varying amounts of platinum. From these measurements, a value of 7 wt.% platinum has been found to be optimal.

(ii) Heat-treatment of platinum-catalyzed carbon substrate

Several authors have studied the effect of heat-treatment on platinized-carbon supports [10 - 12]. We have also examined such an effect on our platinized-carbon substrate. For this purpose, platinized-carbon substrates prepared as above have been subjected to varying periods (0 - 6 h) of heat-treatment at 500 °C in quartz ampoules sealed under a vacuum of $\sim 10^{-3}$ mmHg.

(iii) Preparation of platinized carbon electrodes

Electrodes of various carbon specimens have been prepared by hot pressing the platinized-carbon substrates on expanded platinum metal screens (0.06 mm dia. wire, 1024 mesh/cm²) with 20 wt.% polyethylene powder (average particle size $\sim 5 \mu\text{m}$) as binder. The die assembly containing the mixture of platinized carbon and polyethylene is heated at ~ 140 °C by a heater attached to its platen. An optimum compaction pressure of 50 kg/cm² is applied over the die plunger at this stage and is maintained until the temperature of the die decreased to ~ 90 °C on cooling [1].

(iv) Characterization of platinized carbon substrate using XPS

X-ray photoelectron spectra have been recorded using an ESCA 3-Mark II spectrometer of V. G. Scientific Ltd., U.K. This spectrometer is fitted with a sample preparation chamber having an Ar⁺-etching facility [13]. The sample temperature could be continuously varied between 80 and 900 K. The Au (4f_{7/2}) signal at 83.7 eV is used for energy calibration of the spectrometer.

The recorded spectra have been corrected for background signals using an iterative self-consistent procedure [14], and then analyzed in terms of various possible species of platinum. For this purpose, three or four spectra of metallic platinum have been least-square-error fitted into the background-reduced spectral data by shifting the energy position of each of the component spectra.

(v) Measurement of electrochemical performance of carbon electrodes

The cell used to measure electrochemical performance parameters contains the working electrode, an Hg/HgO, OH⁻ reference electrode equipped with a Luggin capillary, a high surface area flat-bed counter-electrode made from sintered nickel, a magnetic stirrer, and 6M KOH electrolyte. Details of the working electrode holder with gas chamber have been described previously [1].

Galvanostatic polarization studies have been carried out using a regulated d.c. power supply and a high-power-rated rheostat in series with the electrochemical cell. Current-potential curves at room temperature (~ 30 °C) for cathodic reduction of oxygen (medical grade) have been obtained for

all the electrodes described here. The experiments have been repeated with a minimum of two electrodes each time and are found to be reproducible. Life-time tests have been conducted on the optimized electrodes by loading them at current densities ranging from 200 A/m² to 10 000 A/m² over a period of ~1200 h and accompanying changes in electrode potential have been recorded. The potential recovery transients have been obtained for some of the electrodes.

Results and discussion

The characteristics of the electrodes employed during the present study are summarized in Table 1. The types 1 and 2 electrodes have been fabricated from the untreated charcoal substrate. Electron micrographs of these electrodes reveal the fact that they do not possess a suitable pore structure for gas diffusion [1]. On the other hand, the types 3 and 4 electrodes, fabricated from the treated charcoal substrate, have been found to possess visibly uniform pore size distribution over the whole of the electrode surface, which is a desired feature for gas-diffusion electrodes [1]. Current-potential curves for the cathodic reduction of oxygen obtained at the optimum gas pressure of 130 mmHg with the types 1 - 4 electrodes are shown in Fig. 1.

The type-1 electrodes have been found to have limiting currents of about 20 mA/cm² whereas type-3 electrodes can withstand load currents up to 650 mA/cm². In the light of the information gathered on the pore structure from the electron micrographs of these electrodes, the mass-transfer factor seems to be mainly responsible for the polarization of type-1 electrodes. The type-2 electrodes, fabricated by depositing an optimum amount of platinum metal catalyst on the untreated charcoal substrate, have limiting current values close to 50 mA/cm². From the polarization

TABLE 1
Chemical characteristics of electrode substrates

Electrode type	Loss of carbon on gas activation (wt.%)	Pt catalyst content (wt.%)	Duration of heat treatment (h)
1	0	0	0
2	0	7	0
3	66	0	0
4	66	7	0
5	66	7	0.75
6	66	7	1.5
7	66	7	3
8	66	7	4.5
9	66	7	6

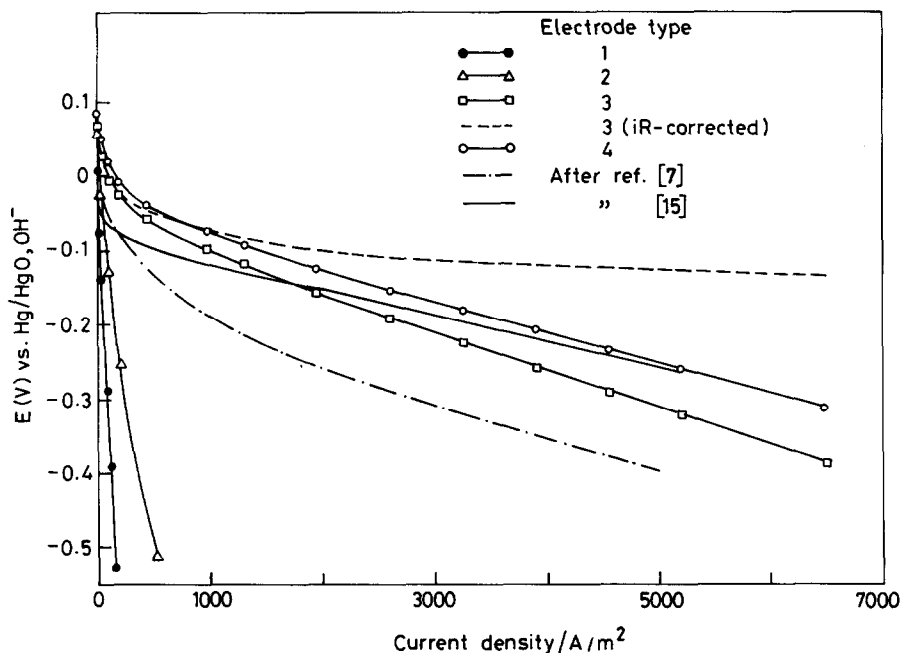


Fig. 1. Current-potential curves for types 1-4 electrodes at oxygen gas pressure of 130 mmHg; iR -corrected curve for type-3 electrode is also included. Curves for Vulcan XC-72 [7] and Norit-BRX [15] carbon-air cathodes are shown for comparison.

curves of types 1 and 2 electrodes, it can be seen that the polarization value for type-2 electrodes at a particular current density is significantly lower than that for type-1 electrodes. This indicates that although the types 1 and 2 electrodes are mainly limited by mass-transfer polarization, the Pt-catalyst present in the substrate of type-2 electrodes does enhance their performance by reducing the charge-transfer polarization.

It has been possible to optimize the mass-transfer polarization component of these carbon gas-diffusion electrodes by tailor-making their porous structure. The polarization behaviour of type-3 electrodes represents such a situation. There is a considerable decrease in the slope of the current-potential curve obtained for the cathodic reduction with type-3 electrodes compared with those curves obtained for types 1 and 2 electrodes. This improvement in the performance of type-3 electrodes could be visualized in the light of the following electrochemical relationship:

$$\eta = -i(R_{ct} + R_{mt,c} + R_{mt,a} + R_{ohm}) \quad (1)$$

where η is the overpotential at a given current density, i ; R_{ct} is the charge transfer resistance; $R_{mt,c}$ and $R_{mt,a}$ are the mass-transfer resistances corresponding to the cathodic and anodic segments, respectively; and R_{ohm} is the effective ohmic resistance which could be attributed to either of the following: (a) resistance of the solution in the carbon powder layers, (b) specific resistance of the carbon powder itself, and (c) contact resistance

among the carbon particles. The contributions from $R_{mt,a}$ and $R_{mt,c}$ to the overpotential could be considered to be negligible owing to the high concentration of the electrolyte (6M KOH) and the negligible effects observed in the polarization behaviour over the current ranges of the study above the oxygen gas pressure of 130 mmHg.

The iR -free current-potential curve for a type-3 electrode obtained from its potential recovery transients is also shown in Fig. 1. The recorded potential recovery transient data for this electrode are shown in Fig. 2. When the current, i , is interrupted, a rapid drop in electrode potential, $E_2 - E_1$, followed by an exponential-like transient is observed. In these data, the ratio, $(E_2 - E_1)/i$, is found to be about 0.3 ohm cm^2 and is nearly independent of i . In such a situation, the drop in electrode potential observed on cutting the currents can be attributed to the iR -drop of the electrode [15]. The electronic resistivity of type-3 electrodes obtained from such measurements is about 6 ohm cm , which is significantly higher than their specific resistivity value of about 0.4 ohm cm [1].

From these data, it is evident that the major contribution to the polarization of type-3 electrodes comes from their ohmic component and, in particular, from the resistance of the solution in the carbon powder layers. Nevertheless, the contribution from the charge-transfer polarization component of these electrodes cannot be ignored. The improvement seen in the polarization behaviour of type-4 electrodes in relation to type-3 electrodes is possibly due to the reduction in both the charge-transfer as well as the ohmic polarization components of the type-4 electrodes owing to the presence of Pt-metal catalyst in the substrate. Figure 1 also includes the data of Scherson *et al.* [7] for a Vulcan XC-72 carbon electrode and that of Iliev *et al.* [15] for a Norit-BRX carbon-based electrode. The electrochemical performance of our types 3 and 4 electrodes is competitive with those reported by these authors.

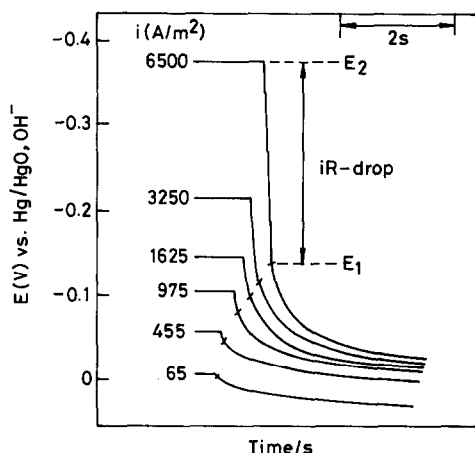


Fig. 2. Potential recovery transients for type-3 electrode.

Current-potential data have also been obtained for electrodes fabricated from a platinized carbon substrate subjected to heat treatment under vacuum for durations ranging from 0 to 6 h. Observed potentials (*vs.* Hg/HgO, OH⁻) for the types 4 - 9 electrodes in 6M KOH at 30 °C at load currents of 5200 A/m² are shown in Fig. 3. Among these, the minimum polarization is seen for the type-7 electrodes. The polarization curve for a type-7 electrode over the current range 0 - 22 000 A/m² is shown in Fig. 4. The values of the exchange current density and Tafel slope for type-7 electrodes are $\sim 3 \times 10^{-4}$ A/m² and ~ 57 mV/decade, respectively, whereas those for type-3 electrodes are $\sim 10^{-5}$ A/m² and 45 mV/decade.

The observed increase in Tafel slope and exchange current density values of type-7 electrodes can be attributed to the increased catalytic activity of the carbon electrodes owing to the presence of highly dispersed Pt-metal. It is noteworthy that the exchange current densities for the oxygen electrode on an effective platinum surface are typically $\sim 10^{-6}$ - 10^{-7} A/m² [16].

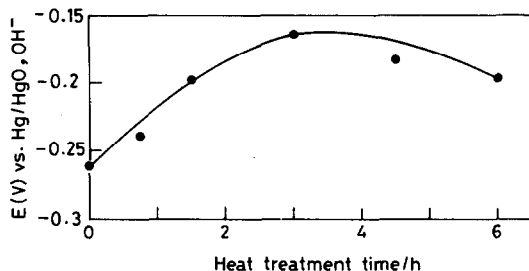


Fig. 3. Observed potentials at load current density of 5200 A/m² for types 4 - 9 electrodes.

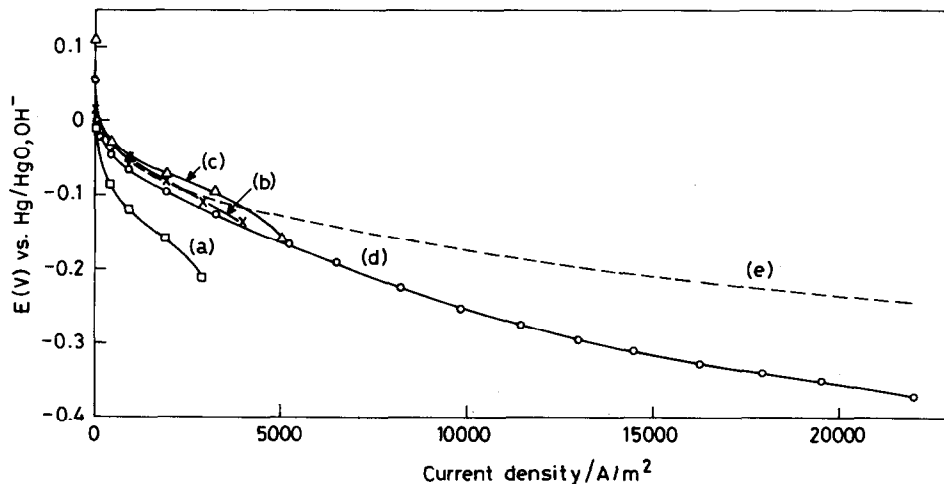


Fig. 4. Current-potential curves for: (a) 10% Pt/RB carbon electrode [18]; (b) 5% Pt/Norit-BRX carbon electrode [15]; (c) 15% Pt/RB carbon electrode [17]; (d) type-7 electrode at oxygen gas pressure of 130 mmHg; (e) type-7 electrode after *iR* correction.

For the purpose of comparison, data for a 15 wt.% Pt/RB-carbon electrode [17], a 10 wt.% Pt/RB-carbon electrode [18], and a 5 wt.% Pt/Norit-BRX carbon electrode [15] for oxygen reduction in concentrated alkali are also included in Fig. 4. It can be seen that the performance of our type-7 electrode (curve (d)) is superior to that of the 10 wt.% Pt/RB-carbon electrode (curve (a)) and is competitive with the performance of both the 15 wt.% Pt/RB-carbon (curve (c)) as well as the 5 wt.% Pt/Norit-BRX carbon (curve (b)) electrodes. An iR -free current-potential curve for our type-7 electrode calculated from its potential recovery transients is also shown in Fig. 4. These potential recovery transient data are shown in Fig. 5. The ratio, $(E_2 - E_1)/i$, is about 0.06 ohm cm² and is nearly independent of i . The electronic resistivity of the electrode calculated from these data is 1.2 ohm cm, which is lower than the corresponding value of 6 ohm cm obtained for the bare carbon electrodes of type-3. This shows that the platinum metal crystallites present in the substrate of type-7 electrodes significantly reduce the ohmic polarization component of the electrodes. These data also support our earlier hypothesis regarding the reduction in charge-transfer and ohmic polarization components of type-4 electrodes.

X-ray photoelectron spectra recorded in the Pt(4f) region of platinum dispersed on treated carbon (sample I), platinum dispersed on untreated carbon (sample II) and platinum metal, are presented in Fig. 6. In our attempts to analyse the Pt(4f) spectra in terms of several Pt species, we have found that there are four Pt components for sample I and have labelled them as 1 to 4 as shown in Fig. 7. Only three Pt components, labelled as 1, 2 and 4, are found for sample II (see Fig. 8). From the binding energies of the components, it is found that the peaks labelled as 2 in Figs. 7 and 8 are due to the platinum metal. The peaks labelled as 4 are present in both samples I and II and have a chemical shift of about 3.2 eV with respect to

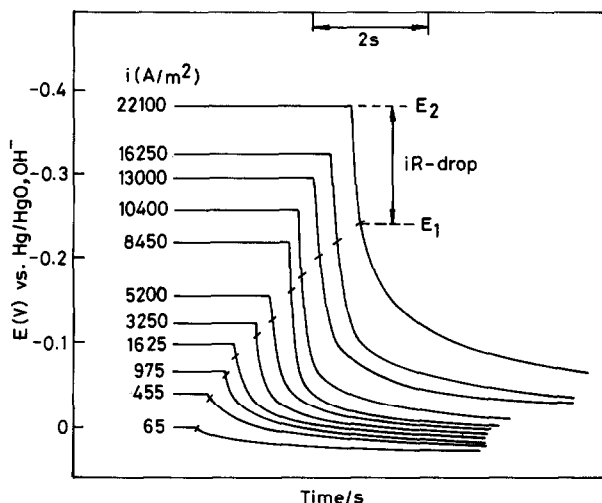


Fig. 5. Potential recovery transients for type-7 electrode.

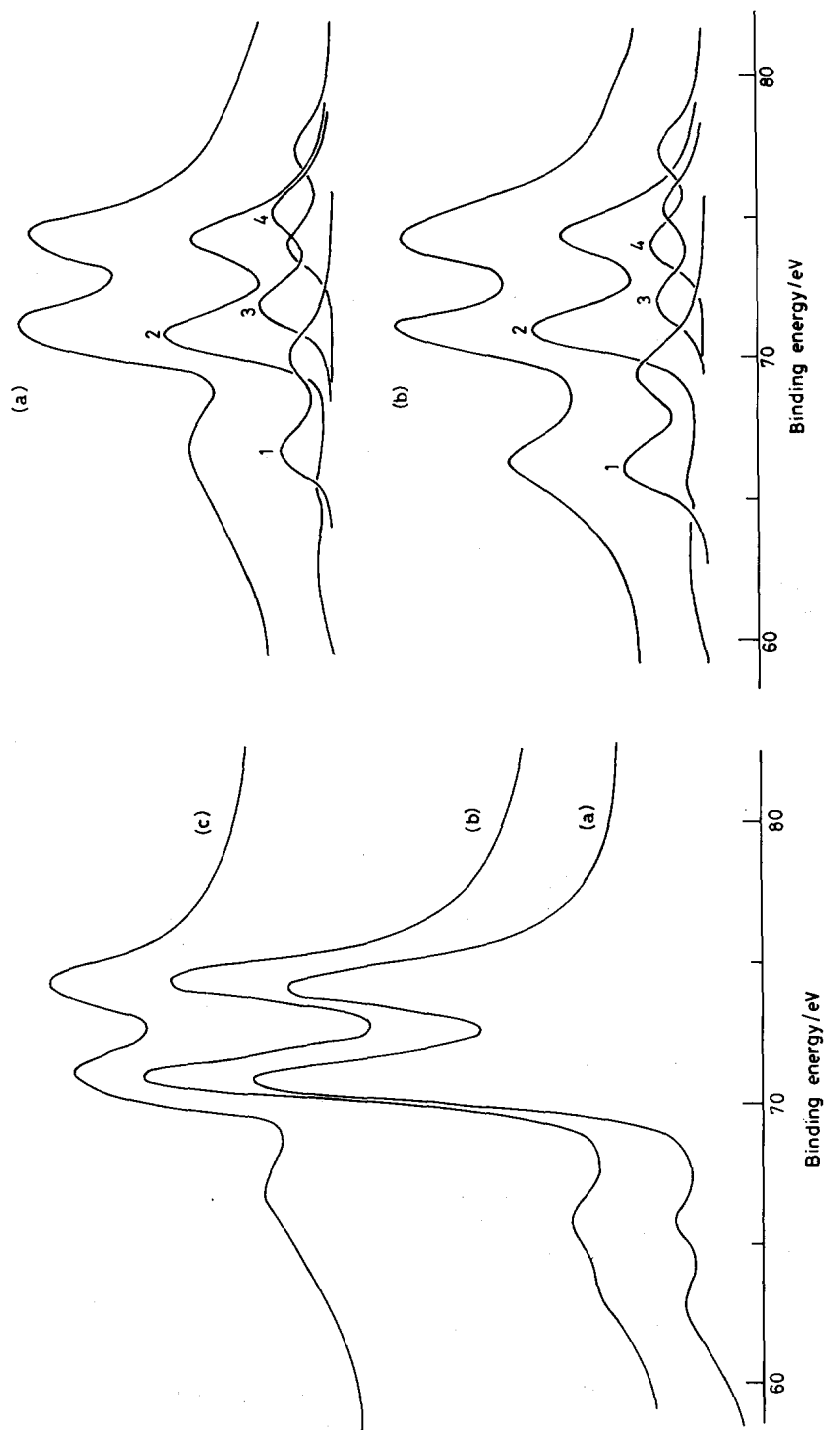


Fig. 6. Room temperature XPS of Pt(4f) region in (a) Pt metal, (b) substrate — type 2, and (c) substrate — type 4.

Fig. 7. XPS of Pt(4f) region of platinized carbon substrate of (a) type 4, and (b) type 7 with the resultant components (labelled as species 1 - 4) of a four component least-square-error fit.

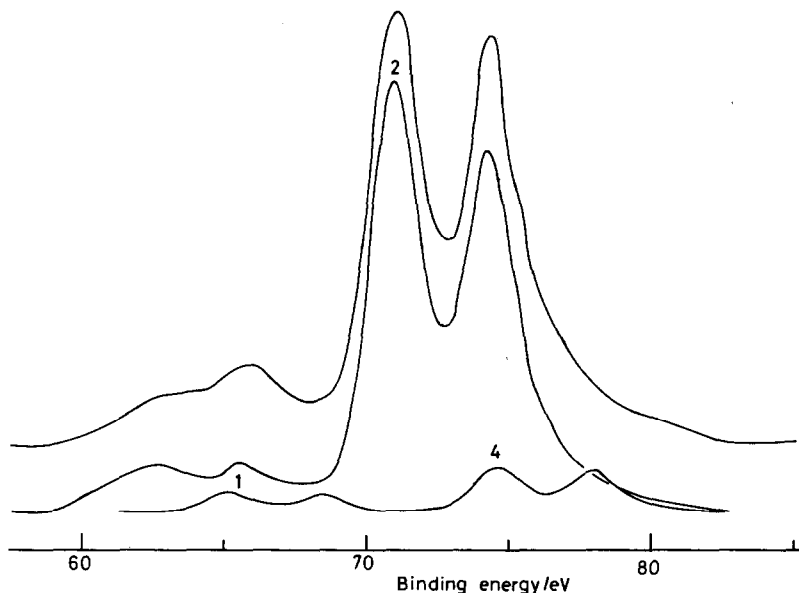


Fig. 8. XPS of Pt(4f) region of a type-2 platinized carbon substrate subjected to heat treatment under vacuum at 500 °C for 3 h. The resultant components of a least-square-error fit are shown as species labelled 1, 2, and 4.

the platinum metal. This, we believe, is an oxidizable impurity of Pt that forms in small quantity in all the samples.

The main difference in the spectra of the two samples arises from the fact that species 1 and 3 are present in the spectra of sample I but are negligible, or totally absent, in the spectra of sample II. This suggests that the enhanced activity of sample I is due to the presence of these species. Species 3 in Fig. 7, with a chemical shift of about 1.2 eV, may be due to the formation of some complex of platinum on the treated carbon [19]. Species 1 is the most unusual in that it shows a very large negative chemical shift of about 5 eV with respect to platinum. Such a negative chemical shift can arise through the transference of electrons from the carbon substrate to the dispersed platinum particles. Indeed, such shifts are known to occur for the active catalytic species in strong metal-support interaction (SMSI) catalysts [20]. However, in this case, the shift is too large to be attributed solely to electron transfer from carbon to platinum particles. Instead, we suggest that species 1 represent very finely-divided platinum particles in close proximity to carbon; this, besides leading to charge transfer, will cause a considerable change in the environment of the platinum particles in the prepared electrode compared with that of the platinum particles in the platinum metal itself. Such an environment might affect the relaxation energy contribution in the chemical shift and thereby lead to a negative value.

According to the above argument, species 1 will be the catalytically active species. To establish this hypothesis and to understand the significance

of species 3, we have carried out a heat-treatment experiment on these samples. Since we found that the electrochemical activity of sample I can be enhanced significantly by its heat-treatment under vacuum at 500 °C for 3 h, we have also heated the samples *in situ* under vacuum at 500 °C for 2, 3, 5, and 9 h, and have recorded the Pt(4f) spectra. We find that while the spectra of sample II do not exhibit any changes with heating, considerable changes take place in the spectra of sample I. As depicted in Fig. 7(a) and (b), we also observe that in the spectra of sample I, the intensity of the peak corresponding to species 3 decreases on heating while that of the peak corresponding to species 1 increases. To identify the importance of the electroactive species, we have plotted (Fig. 9) the relative intensities (in percent.) of peaks corresponding to species 1 and species 3 as the function of duration of heating for sample I. Results show that the intensity of the peak corresponding to species 1 reaches a maximum after 3 h of heating, while that corresponding to species 3 decreases with increase in the duration of heating. These findings suggest that the Pt complex degrades into finely-divided, catalytically active platinum. This supports the hypothesis that species 1 are the catalytically active species. The gradual decrease in the intensity of species 1 on heating beyond 3 h could be attributed to migration of active platinum particles and the formation of metallic clusters of platinum [10].

In the spectra of sample I, the slight decrease observed in the intensity of the peak corresponding to species 2 could be due to the formation of metallic platinum on prolonged heating of sample I and could be responsible for the decrease in electrochemical activity on heating the platinized carbon substrate for periods longer than 3 h. A more elaborate way to corroborate these findings would be to measure the distribution of platinum on the

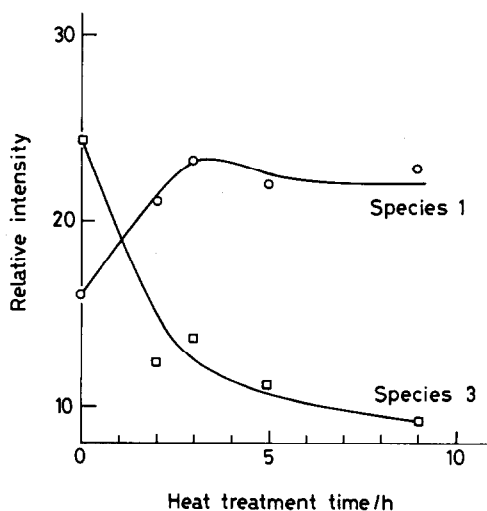


Fig. 9. Relative intensities of peaks corresponding to species 1 and 3 as a function of the duration of heating for treated carbon catalyzed with 7 wt.% platinum.

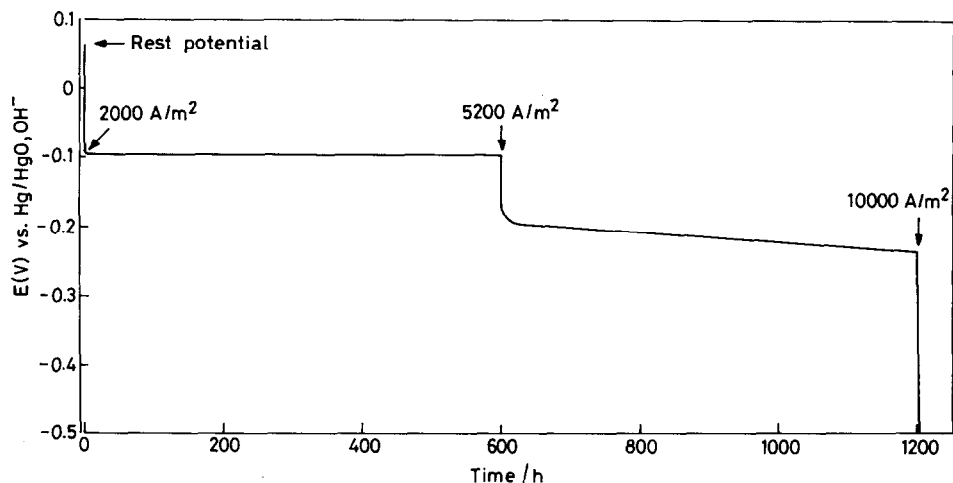


Fig. 10. Operational lifetime curve for type-7 electrode at room temperature ($\sim 30^\circ\text{C}$) and oxygen gas pressure of 130 mmHg.

platinized carbon substrate by BET methods and also to conduct magic angle solid-state NMR studies on these samples.

Type-7 platinized-carbon-air electrodes have been subjected to load tests at current densities of 2000 and 5200 A/m^2 under an oxygen gas pressure of 130 mmHg for ~ 1200 h. The data for these load tests are summarized in Fig. 10. The electrodes show no deterioration over the duration of test at a load current density of 2000 A/m^2 , while a slight deterioration is seen when the load current density is increased to 5200 A/m^2 . On increasing the load current density to 10000 A/m^2 , the electrodes are found to deteriorate within about 2 h. This performance is superior to that reported for other platinized-carbon-air electrodes.

Conclusion

The present study has resulted in the fabrication of high-performance platinized-carbon-air electrodes which can be loaded at current densities of 5200 A/m^2 , without much deterioration, for significantly long durations. A detailed XPS study has been conducted in order to characterise the electroactive species of platinum present on the platinized carbon electrodes. Results indicate that very finely divided platinum situated in close proximity to carbon serves as the catalytically active centre.

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